

# RESERVE COPY, PATENT SPECIFICATION

691924



Date of Application and filing Complete Specification: June 2, 1950.

No. 13818/50.

Application made in Netherlands on June 22, 1949.

Complete Specification Published: May 27, 1953.

Index at acceptance:—Classes 2(iii), V; and 90, B.

## COMPLETE SPECIFICATION

### A Process for Recovering Carotene from Carotene-Containing Oils and Derivatives thereof

We, LEVER BROTHERS & UNILEVER LIMITED, a Company registered under the laws of Great Britain, of Port Sunlight in the County of Chester, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for recovering carotene from carotene-containing oils and derivatives thereof.

It is well known to separate carotene from alfalfa by the steps of extraction followed by chromatography of the extract using activated carbon in the form of carbon black, to preferentially adsorb the chlorophyll and xanthophyll.

However, an analogous process cannot be used for extracting carotene from carotene-containing oils such as palm oil, since the solution obtained by subsequent elution of the activated carbon contains practically no carotene but mainly oxidised carotene.

It has now been found that if carotene is recovered from carotene-containing oils by the chromatographic treatment of the said oils with an adsorbent comprising finely-divided activated carbon which has been freed of oxygen, then on subsequent elution of the activated carbon, a solution is obtained which contains carotene in an unchanged state. This means that a high percentage of the carotene originally present in the oil is extracted. It has also been found that the oil freed of carotene is recovered in a partially bleached state. This oil may be used instead of the original oil for various purposes, such as making margarine.

Thus the present invention provides a process for recovering carotene from

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carotene-containing oils and derivatives thereof which comprises contacting said oil or derivatives with finely-divided activated carbon which has been freed of oxygen and removing the carotene adsorbed in the carbon by any carotene solvent having an eluting action in respect of carotene so adsorbed.

The activated carbon may be freed of oxygen by treating it at normal or at a slightly elevated temperature with a reducing agent such as hydroquinone, formic acid or sodium sulphite dissolved in a suitable liquid such as benzene, ether, alcohol or water. Preferably a solution of hydroquinone in benzene is used. When treating activated carbon with such a solution, the treatment is continued until hydroquinone is detected in the filtrate. Benzene is then used for rinsing the carbon until all the quinone and hydroquinone have been expelled from the carbon. This benzene has then to be expelled from the carbon with petroleum ether or some other fat solvent such as ether or acetone since benzene has an eluting action in respect of carotene.

The activated carbon may also be freed of oxygen by treating it with a gas such as hydrogen, carbon monoxide, nitrogen, steam or carbon dioxide at a temperature above 350° C. Preferably temperatures between 400° C. and 500° C. should be used. Any increase of temperature above 500° C., however, does not give a better effect.

The above described treatment of the carbon results in an activated carbon having a good adsorptive capacity towards carotene dissolved in oil or derivatives thereof.

All kinds of activated carbon are suitable for carrying out the process of the

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invention and those known commercially under the Registered Trade Name "Norit" are particularly suitable. Carbon black, however, is less suitable since its capacity for adsorbing carotene is lower than in the case of many other activated carbons.

The process may be used for separating carotene from such carotene-containing oils as palm oil or the oil from carrots "*Daucus Carota*." It may also be used for separating carotene from carotene-containing derivatives of such oils, for example, free fatty acids or from mixtures of these derivatives with oils.

The oils may be treated as such with the carbon in which case it is often advisable to work at a moderately elevated temperature sufficient to reduce the viscosity of the oil. Alternatively, the viscosity may be reduced by diluting the oils with a solvent such as petroleum ether, acetone or ether.

Preferably the oil is deaerated prior to treatment with the carbon and care should be taken to ensure that the carbon, when freed of oxygen, is prevented from coming into contact with oxygen either before, during or after adsorption to avoid oxidation of the carotene during treatment. In many cases, the gas adsorbed in the carbon after the heat treatment mentioned above, gives sufficient protection against oxygen. If these conditions are observed, the carbon can be used many times for extracting carotene by treating it anew with oil after elution. Alternatively, it may be treated with a fat solvent after elution and then treated anew with oil. After the desired quantity of oil has been placed in contact with the carbon, the carbon, if desired, may be freed of fat with a non-eluting solvent before the carotene is eluted.

The carotene adsorbed on the carbon is recovered by eluting the carbon with an organic liquid and it is preferred to use an aromatic hydrocarbon such as benzene, toluene or xylene. It has been found that the effectiveness of elution is improved the more and/or the longer the side chains possessed by the aromatic hydrocarbon solvent. This solvent may be used again and again for elution until a sufficient concentration of carotene has been obtained. The carotene can be recovered in a pure state from the carotene-containing solution obtained in this way, or may be obtained in the form of a concentrated solution in oil. Such a concentrated solution is very useful for addition to margarine. The adsorption of the carotene and its subsequent elution may be effected either in batches or con-

tinuously by the method described in our co-pending application No. 26171/49 (Serial No. 691,355).

The invention will now be illustrated by means of the following examples:—

#### EXAMPLE 1.

A suspension of 1 part of "Norit" Pc3 in benzene is poured into a column and the benzene run off so that the Norit forms a coherent mass in the column, the diameter to length ratio of which is 1:2. Benzene saturated with hydroquinone is then conducted through the column until hydroquinone is detected in the filtrate. The quinone in the column is removed by rinsing the column with benzene and the benzene retained by the column is replaced by petroleum ether.

A solution of 1 part of Bissao palm oil containing 1.11 milligrammes of carotene per gramme in 1.5 parts petroleum ether is now introduced into the column. The solution of oils leaves the column partly bleached. The column is then rinsed with petroleum ether until practically no oil is detected in the filtrate.

The carotene retained by the column is washed from the carbon with 15 parts of benzene. It is found that 66.5% of the carotene contained in the original oil is recovered therefrom.

When the same process is carried out with "Norit" which has not been freed of oxygen, the carotene is adsorbed but on washing out the column a reddish orange solution in benzene is obtained and this solution contains no trace of carotene since all the carotene has been transformed by oxidation into other products.

#### EXAMPLE 2.

One part of "Norit" is heated for half an hour at 400° C. in an atmosphere of carbon dioxide or hydrogen. It is allowed to cool and when cool placed in petroleum ether. The carbon and petroleum ether is then placed in a column having the same dimensions as that of Example 1. Two parts of red palm oil with a carotene content of 1.11 milligrammes per gramme dissolved in 1.5 parts of petroleum ether is then introduced into this column and then the oil is rinsed from the column with five parts of petroleum ether. The carotene in the column is washed from the carbon with 20 parts of benzene and it is found that 72% of carotene in the original oil is recovered.

If the same procedure is followed, but 12 parts of toluene is used for washing the carotene from the column, 78% of the carotene in the original oil is recovered and when 8 parts of commercial xylene is used for washing out, 86%

of the carotene is recovered, indicating that a better extraction of carotene from the column is achieved with 12 parts toluene and 8 parts xylene than with 20 parts benzene.

What we claim is:—

1. A process for recovering carotene from carotene-containing oils and derivatives thereof which comprises contacting said oil or derivatives thereof which comprises contacting said oil or derivatives with finely-divided activated carbon which has been freed of oxygen and removing the carotene adsorbed on this carbon by any carotene solvent having an eluting action in respect of carotene so adsorbed.

2. A process as claimed in Claim 1 in which a solution of said oil or derivative in an oil-solvent is contacted with the carbon.

3. A process as claimed in Claim 2 in which said oil is palm oil.

4. A process as claimed in Claim 3 in which said oil-solvent is petroleum ether.

5. A process as claimed in any of the claims 2 to 4 in which said solution is passed through a column of activated carbon and the carotene is eluted from this column with the carotene solvent.

6. A process as claimed in any of the preceding claims in which the carotene adsorbed on the carbon is eluted therefrom with an aromatic hydrocarbon.

7. A process as claimed in Claim 6 in which said aromatic hydrocarbon is benzene.

8. A process as claimed in Claim 6 in which said aromatic hydrocarbon contains one or more side chains.

9. A process as claimed in Claim 8 in which said aromatic hydrocarbon is toluene.

10. A process as claimed in Claim 8 in which said aromatic hydrocarbon is xylene.

11. A process as claimed in any of the preceding claims in which the carbon is freed of oxygen by treating it with a reducing substance.

12. A process as claimed in Claim 11 in which said reducing substance is hydroquinone.

13. A process as claimed in any of the claims 1 to 10 in which the carbon is freed of oxygen by heating it in a gas such as carbon dioxide or hydrogen at a temperature of at least 350° C.

14. A process for separating carotene from carotene-containing oils substantially as herein described.

15. Carotene when separated from carotene-containing oils by the process claimed in any of the preceding claims.

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